D. Development of Technology for Removal of PCBs and Other Substances of Concern (SOCs) from Shredder Residue

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The Polyurethane Recycle and Recovery Council (PURCC) is also participating and cost-sharing in this project.
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Objective

- Develop viable strategies and technology for the control and minimization or elimination of polychlorinated biphenyls (PCBs) and other substances of concern (SOCs) from recycled automotive materials.

Approach

- Identify efficient and environmentally acceptable process solutions for removal of contaminants, including PCBs from materials recovered from shredder residue.
- Conduct large-scale washing/cleaning tests using plastics from shredder residue in commercially available equipment.
- Identify necessary modifications to existing equipment to improve its performance and/or economics.
- Examine variances in analytical procedures/test results for PCB analysis.

Accomplishments

- Completed bench-scale screening of 11 surfactants and 3 organic solvents for removal of PCBs and other contaminants from polymers derived from shredder residues and specified preferred surfactant/cleaning solutions.
- Reviewed and identified commercially available washing equipment that can be adapted to a commercial-scale recycle process.
- Conducted trials of selected equipment; performed analyses of samples of cleaned product.
- Conducted laboratory tests to develop an understanding of the variability inherent in the analytical procedures for PCB analysis.

Future Direction

- Complete the large-scale cleaning tests using commercially available equipment and systems.
- Identify necessary modifications to existing equipment for most efficient and economical operation.
- Prepare a cost analysis of modified systems.
- Complete laboratory tests to quantify variability in PCB analytical procedures.

Summary

The objective of this project is to develop techniques and/or technology to identify and/or cost-effectively remove polychlorinated biphenyls (PCBs) and other substances of concern (SOCs) from recycled automotive materials.

SOCs can impact the recyclability of automotive materials in a number of ways. Certainly, their presence in either recycled materials and/or materials source stream impact the overall costs of recovering recyclable materials. In some cases, their presence at parts-per-million levels, such as PCBs, can prevent the reuse of the recovered materials such as polymers and polyurethane foams.

The strategy that is required for control of the SOCs may vary regionally. For example, requirements are different in Europe, North America, and Asia for various SOCs. Strategies for control of SOCs can also depend on the technology that is being proposed for recycling the automotive material.

The presence of SOCs in current vehicles and/or in other durable goods that are presently recycled with end-of-life vehicles is likely to impact the materials recycle stream for the foreseeable future. Consequently, control of certain SOCs will require technology that will effectively remove the SOCs from recovered materials consistent with current regulatory requirements and consistent with the market requirement for the recovered material.

The initial focus of the work in this project is on the development of options and technology for removal of PCBs from potentially recyclable materials recovered from shredder residue. PCBs, at parts-per-million levels, are routinely found in shredder residue. The source of the PCBs is not completely understood but historically has been associated with liquid PCB-containing capacitors and transformers that inadvertently escape the scrap inspections and control process at the shredders.

Bench-scale screening of commercially available surfactants and large-scale testing of commercially available equipment for cleaning of recovered materials has been conducted.

Laboratory experiments have also been performed to develop an understanding of the variability in PCB analytical procedures.

Bench-Scale Screening of Commercially Available Surfactants for Removal of PCBs

Working with Argonne, Troy Polymers, Inc. (TPI) completed the bench-scale screening of 11 surfactants and 3 organic solvents for removal of PCBs and other contaminants from polymers derived from shredder residue. Multiple samples of mixed plastics and polyurethane foam that were recovered from shredder residue were used in the study.

The surfactant TRITON RW 50 was found to be the most efficient surfactant among the ones tried. PCB concentrations in the plastics and foam samples that were washed with this surfactant were reduced to below 2 ppm (Table 1).

The three organic solvents were also effective but were precluded from further consideration due to environmental considerations and cost.

Evaluation and Testing of Commercially Available Equipment

Technologies that can potentially be adapted for cleaning/washing of plastics from shredder residue fall into three major categories:

1. conventional methods that include mechanical transport of material through a cleaning solution through an agitation and/or scrubbing process by rotating drums and/or auger systems,
2. ultrasonic systems with and without agitation, and
3. centrifugal systems.

TPI undertook a review of the commercially available equipment, including the following:

- GraPar Corporation, Warren, Michigan. The company's expertise is in the design and manufacturing of aqueous cleaning equipment and systems.
- Almco, Inc., Industrial Finishing Systems, Albert Lea, Minnesota. The company's expertise is in the design and manufacturing of aqueous washers, dryers and liquid filtration systems).
- CarolMac Corporation, Greenville, North Carolina. The company markets centrifuge washers built by SeKoN, Bergamo, Italy.
- RANSOHOFF, Cincinnati, Ohio. The company's expertise is in the design and manufacturing of agitating ultrasonic washers.
- RG Hanson Co., Inc., Bloomington, Indiana. This is a testing lab for developing cleaning specifications and selecting cleaning equipment.
- JTW International, Inc., Lawrenceville, Georgia. The company's expertise is in the design and manufacturing of size reduction, separation, cleaning, and preparation of postconsumer plastic scrap.
- Greco Brothers Incorporated, Providence, Rhode Island. The company's expertise is in the design and manufacturing of aqueous ultrasonic cleaning systems.
- MTA Technical Cleaning, Reseda, California. The company's expertise is in the design and manufacturing of aqueous and ultrasonic parts cleaning equipment.
- Sanborn Technologies, Walpole, Massachusetts. The company's expertise is in the design and manufacturing of separation, ultra-filtration and nano-filtration and in fluid management and disposal issues.
- SeKoN, Italy. The company's expertise is in the design and manufacturing of aqueous washing using centrifugation equipment.

Table 1. Concentration of PCBs in plastics and foam before and after washing, bench-scale tests for surfactant selection

Designation	PCBs before washing (ppm)	
Plastics	2.8 ± 1.4	
Foam	27.2	
Surfactant or solvent used	PCBs in plastics after washing (ppm)	PCBs in foam after washing (ppm)
Triton DF-12	<1	2.4
Triton RW-100	<1	2.7
Tergitol TMN-6	<1	4.1
Bio-Terge Pas-8S	3.2	6.0
Triton RW-50	<0.08	2.0
Triton RW-75	—	4.7
No surfactant used	—	6.2

Preliminary large-scale cleaning/washing experiments were conducted using plastics from shredder residue in the following equipment to identify the limitations of various types of existing equipment: ALMCO rotary drum washer, equipped with a dryer, and SeKoN centrifuge equipment. The tests were carried out on approximately 100 lb of plastic chips each. The particle sizes were between 0.2 and 0.5 in. In each of these large tests, the washed material was "visually" clean as far as dirt and oils are concerned. However, the results for the PCB analyses indicated that the tests were not successful in meeting targets for residual concentrations under the test conditions (residence times, surfactant loading). Analysis of residual heavy metals is not yet complete.

Evaluation and testing of the commercially available equipment, to date, suggests that existing equipment may require modification to efficiently and economically clean plastics that are recovered from shredder residue.

Modifications that are suggested are intended to address two issues: (1) the dirt and oil are not evenly distributed on the plastics; (2) plastics are generally hydrophobic in nature and therefore have the tendency to re-adsorb oils and other organics. Key modifications involve (1) ensuring that the washed material does not come in contact with the liberated oil and dirt that is floating on or dispersed in the wash tank, as the washed material is removed from the tank; (2) ensuring that adequate agitation is provided so that the heavier plastics that will tend to sink stay afloat to achieve adequate mixing and contact between the plastics and the washing solution in the tank; (3) ensuring rapid and adequate removal of the oils and dirt from the wash solution to minimize or eliminate readsorption on the plastics; and (4) rinsing of the washed plastics as they exit the wash tank.

Based on these considerations, GraPar Corp. built a pilot-scale test stand. Controlled tests are planned in the GraPar machine at TPI to further delineate the issues (e.g., surfactant loading, residence times, etc.) with regard to effective cleaning of recovered materials so that more effective evaluations of commercially available equipment can be undertaken.

Evaluation of the Variability of PCB Analytical Procedures

In the large-scale washing tests, there was a significant degree of apparent inconsistency in the analytical results of residual PCB concentrations on the washed materials. Evaluation of these results suggested that this variability may be due to a number of factors including

1. sample size,
2. plastics particle size,
3. PCBs extraction procedure,
4. analytical procedures, and
5. interference from other compounds.

To begin an investigation of the effect of these factors, a series of controlled laboratory experiments were conducted at TPI, to investigate sample size, extraction procedures, plastics particle size, and analytical procedures.

In these experiments, samples of plastics were sent for direct PCB analysis to three different laboratories. Split samples of about 300 g each were extracted in hexane at TPI, and the resultant extract was analyzed for PCB concentrations. Typically, analysis of materials for PCBs is done using samples of only few grams of material.

The split samples were extracted with hexane nine times each in exactly the same manner. Three equivalent sets of these samples were then analyzed by three different laboratories using standard PCB analysis techniques. Preliminary results follow:

1. The three laboratories produced fairly consistent results for each set of samples.
2. Direct analysis of the samples, from the three labs showed that the PCBs concentration in the granulated plastics was about 5 ppm, while the concentrations reported for the ungranulated samples were about 10 ppm. Because the granulated samples have larger surface area per unit mass than the other samples, a more efficient extraction of PCBs from the plastics would be expected in the case of the granulated chips. These apparently inconsistent results are an indication of the variability that can be encountered with direct analysis of the plastics.

3. Calculation of the PCBs concentration in the 300-g samples based on hexane extractions showed concentrations of PCBs in the granulated samples to be comparable to the ungranulated samples. These results indicate that the PCB contamination is a surface contamination and that the PCBs have not been absorbed below the surface of the plastics.

Two of the laboratories identified Aroclor 1242 as the only PCB present, while the third laboratory identified Aroclors 1232 and 1254 as the only two present, and all three labs reported about same overall PCB concentrations. Each of these Aroclors consists of a multiple of congeners, and assignment of the PCB to a particular Aroclor is based on the measured distributions of specific congeners present as interpreted by the analysts. This is an indication of the complexity of the PCB analysis in these samples.

Analyses of samples using GC-ECD (gas chromatography-electron capture detector) and GC-MS (gas chromatography-mass spectroscopy) methods were conducted to compare these techniques. Results from the two methods are in good agreement, even though the GC-MS method seems to consistently predict slightly higher values.

Based on the results of these experiments, the cooperative research and development agreement (CRADA) team is planning a seminar to discuss PCBs analysis with expert chemical analysts to determine whether further work is needed or recommended with regard to analytical procedures.